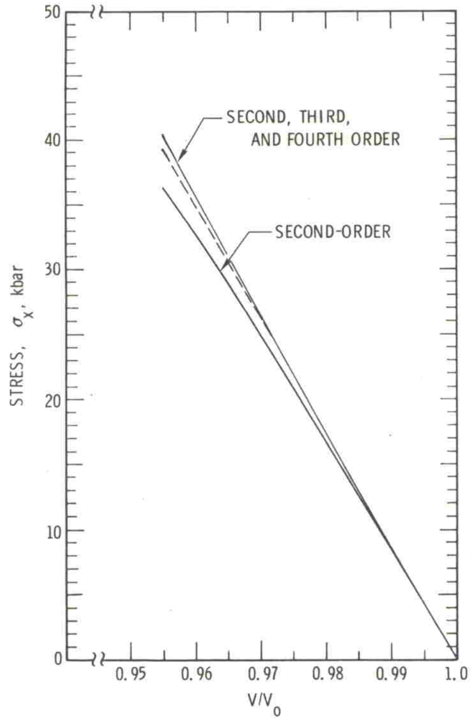

FIG. 5. Stress–vs–relative-volume relation which describes the elastic compression of X-cut quartz. The observed data are best fit by the line which includes second-, third-, and fourth-order constants. To illustrate the contributions of the various constants, the calculated stress-volume relation for the second-order constant alone is shown along with that of the second- plus third-order constant (dashed line).

shows the same coefficients as those obtained over the entire strain range. This observation indicates that the conductivity at the higher strains did not mask any unusual change in the piezoelectric response.

Determination of high-order elastic constants from elastic-shock-compression data is fully described in a recent paper[8] describing similar measurements for sapphire and fused quartz. The present paper follows the methods previously developed to accomplish a fit to the stress-vs-compression data which is obtained from the shock-velocity–particle-velocity measurements. In the data analysis, each shock-velocity–particle-velocity pair is used to compute a stress linear compression point from the conservation of momentum and mass, Eqs. (11) and (12). These data are then fit to a finite-strain constitutive relation by a method of successive approximations. At any particular strain the thermodynamic tension includes contributions from all the coefficients; however, the individual contributions can be separated provided experiments are accomplished over a wide range of strain. In the present case, the various t_1 values range from those for which the second-order constant represents the only detectable contribution, to those in which both the second- and third-order constants represent the only detectable contribution, to those in which second-, third-, and fourth-order constants all cause significant contributions. Thus, even though a single experiment cannot provide unique values for all coefficients, the complete set of experiments provides unique values for all coefficients since the experiments include the entire range of compression for which the various contributions are experimentally significant.

The present experiments lead to the stress–vs–relative-volume relations shown in Fig. 5. The contribution of the various constants is illustrated by separating the response into the contributions from the second-order coefficient alone, the second- plus third-order coefficient, and the observed stress–vs–relative-volume relation which is fit by the second-, third-, and fourth-order coefficients. The finite-strain elastic constants which fit the data are

$$c_{11} = (+0.868 \pm 0.0095)\times 10^{12}\ \mathrm{dyn/cm^2},$$

$$c_{111} = (-3.0 \pm 0.3)\times 10^{12}\ \mathrm{dyn/cm^2},$$

$$c_{1111} = (+75 \pm 25)\times 10^{12}\ \mathrm{dyn/cm^2}.$$

VI. DISCUSSION

Nonlinear acoustics and nonlinear interactions among acoustic,[3] optical,[36] and electrical fields[4] are ordinarily concerned with expressions for nonlinear properties evaluated as derivatives taken near the unstrained position. In that situation the nonlinear constants can be related to the fundamental lattice dynamical anharmonic effects. Typical experiments to evaluate high-order elastic constants, for example, are accomplished at strains less than about 10^{-4}. Since the maximum strains in the ultrasonic experiments are small, the nonlinear properties are expected to be representative of states at the unstrained condition.

The very large elastic limit which X-cut quartz exhibits under shock-wave compression allows the present measurements to be accomplished at large ($>10^{-4}$) strains. Nonlinear contributions which are small and difficult to detect under acoustic conditions are substantial and relatively easy to measure under elastic shock-compression conditions. The smallest strains of the present work are larger than those ordinarily employed in acoustic measurements; as such, the present measurements extend acoustic measurements of nonlinear properties by several orders of magnitude in strain. Even though the present measurements represent the response of the solid at the large strains employed in the investigations, it is only through comparison to linear and nonlinear acoustic values that smooth

TABLE I. Piezoelectric stress constant e_{11} (C m^{-2}). (± indicates standard error).

Bechmann (1958)[a]	0.171
Koga *et al.* (1958)[b]	0.174
Graham *et al.* (1965)[c]	0.174 ± 0.003
Present work	0.1711 ± 0.000 94

[a]Reference 21. [b]Reference 37. [c]Reference 11.

extrapolation to the unstrained state can be finally assured.

While the maximum strain employed in the present investigation is substantial (4.3×10^{-2}), it is not massive; hence, one would hope that in many cases the conditions are characteristic of continuous changes from the unstrained position. In fact, any observed deviation from a continuous change is cause for considerable concern since the discontinuous behavior could possibly be a result of inelastic effects.

Some evidence for a discontinuous change in piezoelectric polarization with strain was observed in the previous investigation of the piezoelectric properties of shock-loaded *X*-cut quartz.[11] Contrary to the previous observations, the present investigation, conducted with improved accuracy and better controlled experimental conditions, shows a continuous increase of polarization with strain.

A. Piezoelectric Constitutive Relation

1. Linear Piezoelectric Stress Constant

The continuously increasing piezoelectric polarization shown in the present investigation indicates a smooth extrapolation to zero strain. Inspection of Fig. 4 demonstrates that the nonlinear piezoelectric polarization produces a negligible contribution at the lowest strains; as the strains increase, the nonlinear contribution increases smoothly from the low-strain values. The smoothly increasing polarization combined with the excellent precision of the measurements are strong evidence that the linear constant obtained is representative of conditions at the unstrained state.

The linear piezoelectric stress constant e_{11} obtained in the present investigation is compared to values obtained by previous investigators in Table I. The present work provides the most accurate value achieved to date. The measurements provide values with a standard error of 0.55%. The maximum experimental error does not exceed ± 1%.

Previous authors have utilized the elastic-shock-compression technique to determine the piezoelectric current response of *X*-cut quartz at reduced[38] and elevated temperatures.[39] Even though these measurements are not as complete as those reported in the present investigation and smooth extrapolation to the unstrained state is somewhat uncertain, the data of the present paper give some confidence in the extrapolation. The values obtained by analyzing the data with the present model are shown in Table II.

Over the temperature interval 295–573 °K, a temperature coefficient of $\Delta e_{11}/e_{11}\Delta T = -1.5\times10^{-4}$ °C^{-1} is obtained. This value should be compared to the small-signal measurement[30] of -1.6×10^{-4} °C^{-1} from 288 to 319 °K. Between 295 and 790 °K the elastic-shock-compression measurements show a value of $\Delta e_{11}/e_{11}\Delta T = -1.6\times10^{-4}$ °C^{-1}.

2. Nonlinear Piezoelectric Stress Constant

The nonlinear piezoelectric stress constant for the direct piezoelectric effect, $\partial e_{11}/\partial\eta_1$, is the most unique measurement reported in the present paper. The present measurements provide the first quantitative value for the strain dependence of a piezoelectric constant in any solid. Nonlinear piezoelectric constants are of particular interest at present because of microwave acoustical studies of piezoelectric solids.[4,40] Furthermore, acoustic second-harmonic generation at microwave frequencies[41] and surface-wave microwave responses[41,42] may be utilized to detect nonlinear piezoelectric response. Recently, microwave surface-wave experiments have been employed to determine values for the combined nonlinear elastic, piezoelectric, and dielectric surface-wave contributions in several materials.[43]

Based on the present model the data from the previous elastic compression study at room temperature[11] can be analyzed to yield a value for the nonlinear constant. The value obtained is $\partial e_{11}/\partial\eta = -2.94\pm0.25$ C m^{-2}. Although the standard error is appreciable, 8.5%, the value is in reasonable agreement with the present value (-2.64 ± 0.048). The nonlinear constant can also be compared to that obtained from the acoustic second-harmonic-generation experiments of Carr and Slobodnik,[44] who estimated the constant to lie between -0.5 to -7 C m^{-2}. This order-of-magnitude estimate is in agreement with the present value.

The Maxwell relations for a piezoelectric solid[4,45] can be employed to demonstrate that $\partial e_{11}/\partial\eta_1 = -\partial c_{11}/\partial E_1$. Although the recent realization[17–19]

TABLE II. Piezoelectric stress constants at various temperatures (C m^{-2}). (± indicates standard error.)

Temperature (°K)	e_{11}	$\frac{\partial e_{11}}{\partial\eta_1}$	Reference
79	0.177 ± 0.003	−1.1 ± 0.15	a
295	0.1711 ± 0.000 94	−2.64 ± 0.048	Present work
573	0.164 ± 0.0024	−2.8 ± 0.24	b

[a]Computed from the data of Jones (Ref. 38).
[b]Calculated from the data of Rohde and Jones (Ref. 39).